ENDOCRINE DISRUPTORS FROM COMBUSTION AND VEHICULAR EMISSIONS: IDENTIFICATION AND SOURCE NOMINATION

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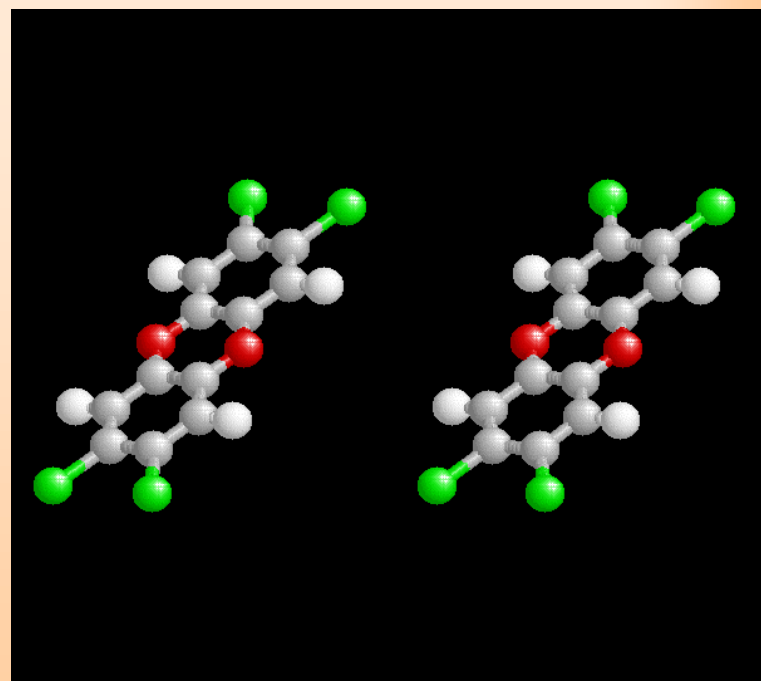**[4]University of Dayton Research Institute, 300 College Park, Dayton, OH 45469**
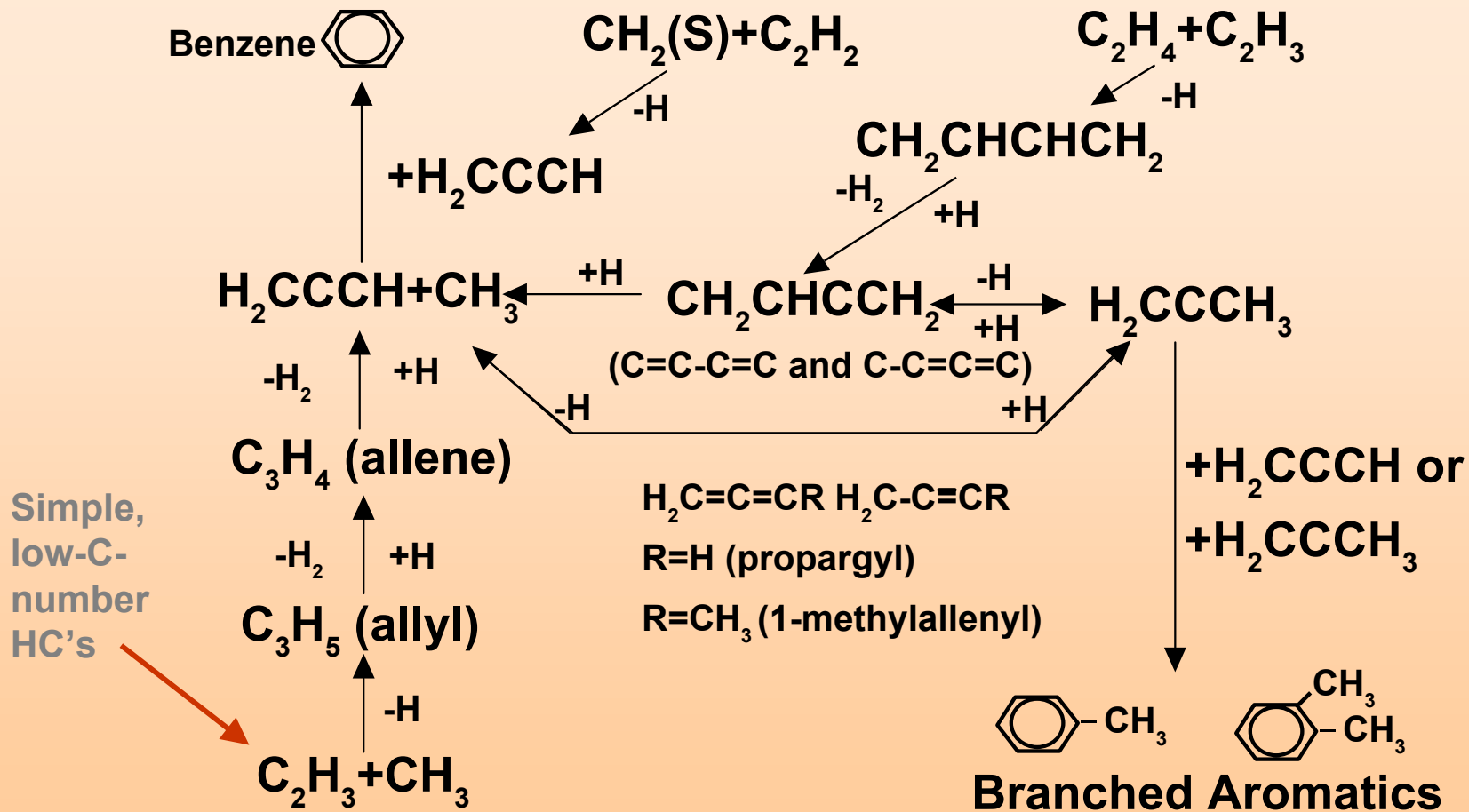***919-541-1534, 919-541-0554 (fax), gullett.brian@epa.gov**

BACKGROUND

- A significant fraction of organic emissions from combustion sources remains uncharacterized
- 100's of compounds are emitted
  - e.g., PAHs, oxygenates, alkyl phenols
- We only see what we specifically look for
  - e.g., PCDD/Fs "dioxins"
- EDCs are emitted from combustion sources
  - e.g., PCDD/F, PCB, Hg
- Combustion sources are ubiquitous
  - constitute a major exposure source

GAS PHASE, AROMATIC PRECURSORS –
How do we get complex aromatic structures?

Benzene

$CH_2(S)+C_2H_2$

$C_2H_4+C_2H_3$

-H

-H

$+H_2CCCH$

$CH_2CHCHCH_2$

$-H_2$ +H

$H_2CCCH+CH_3$ +H CH_2CHCCH_2 $\overset{-H}{\underset{+H}{\longleftrightarrow}}$ H_2CCCH_3

(C=C-C=C and C-C=C=C)

$-H_2$ +H

-H +H

C_3H_4 (allene)

Simple, low-C-number HC's

$H_2C=C=CR$ $H_2C-C=CR$

$+H_2CCCH$ or

$+H_2CCCH_3$

R=H (propargyl)

$-H_2$ +H

R=CH_3 (1-methylallenyl)

C_3H_5 (allyl)

-H

$C_2H_3+CH_3$

$\langle\!\bigcirc\!\rangle$–$CH_3$ $\langle\!\bigcirc\!\rangle\overset{-CH_3}{\underset{-CH_3}{}}$

Branched Aromatics

OBJECTIVE

We will survey combustion sources for potential endocrine disruption activity, try to isolate the compounds responsible for such activity, and attempt to estimate their emission factors.

APPROACH

- Opportunistic combustion source sampling
  - domestic waste burning, diesel trucks (HDDVs), forest fires, fireplaces, and woodstove….others.
- Bioassays
  - Yeast estrogen assay
  - CALUX
  - Vitellogenin mRNA Assay
- Sample fractionation to isolate target compounds
  - HPLC technique (L. Brooks)
  - Capillary Electrophoresis
  - TIE method (G. Ankley)
- Multi Dimensional Gas Chromatography
  - diagram/description
- QSAR, Statistical analyses
  - Structure clues

Source Characterization

- Done
  - diesel truck
  - woodstove
  - sewage sludge incinerator
  - domestic waste

- Future
  - pine straw
  - structural fires
  - oil spill fire
  - municipal waste, full scale
  - DoD diesel truck

On-Road Diesel Sampling

On-Road Diesel Dioxin Sampling Train

- Heated Filter Box
- Filter
- Glass Tube
- Exhaust
- T
- P
- Plastic Nut with Teflon Washer
- ½ Inch Teflon Tubing
- SS Water Jacket
- Ice Water
- T
- XAD-2 Module
- Water Knockout
- High Volume Vacuum Pumps
- Pump
- Pump
- Orifice
- Dry Gas Meter
- SiO₂
- V
- Cooler
- Ice Bath
- Coiled SS Tubing

Legend:
- T Thermocouple
- P Differential Pressure Transmitter
- V Vacuum Gauge
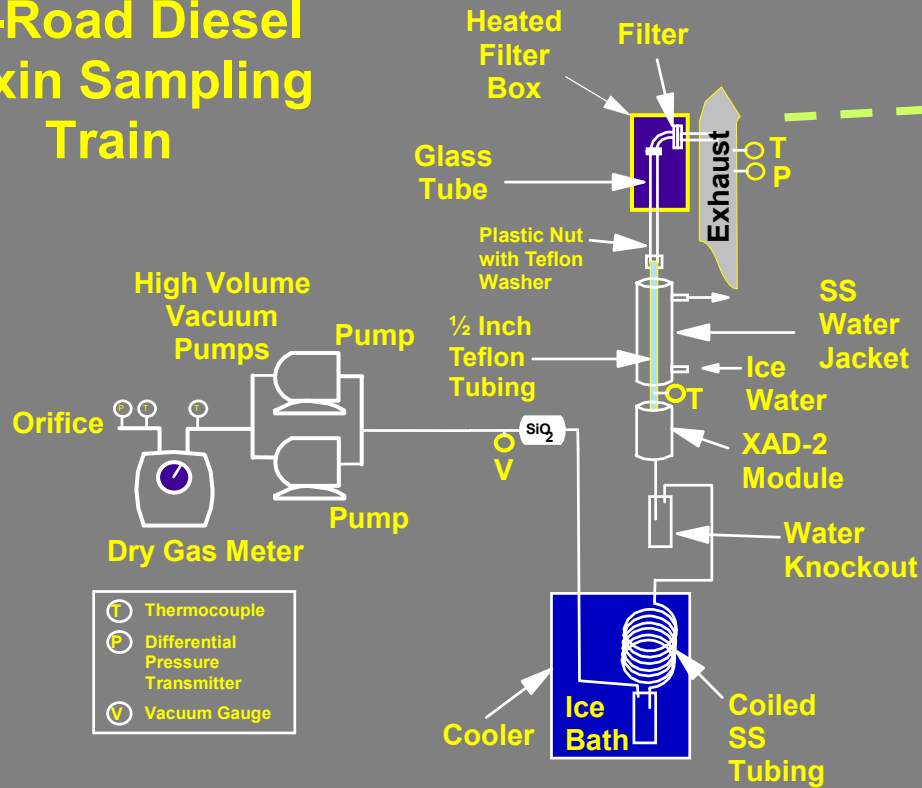
"Uncontrolled" Burning Sources

Burning of Domestic Waste

Wheat Straw Testing

CA PCDD/F, PCB Sources?

FIREPLACE
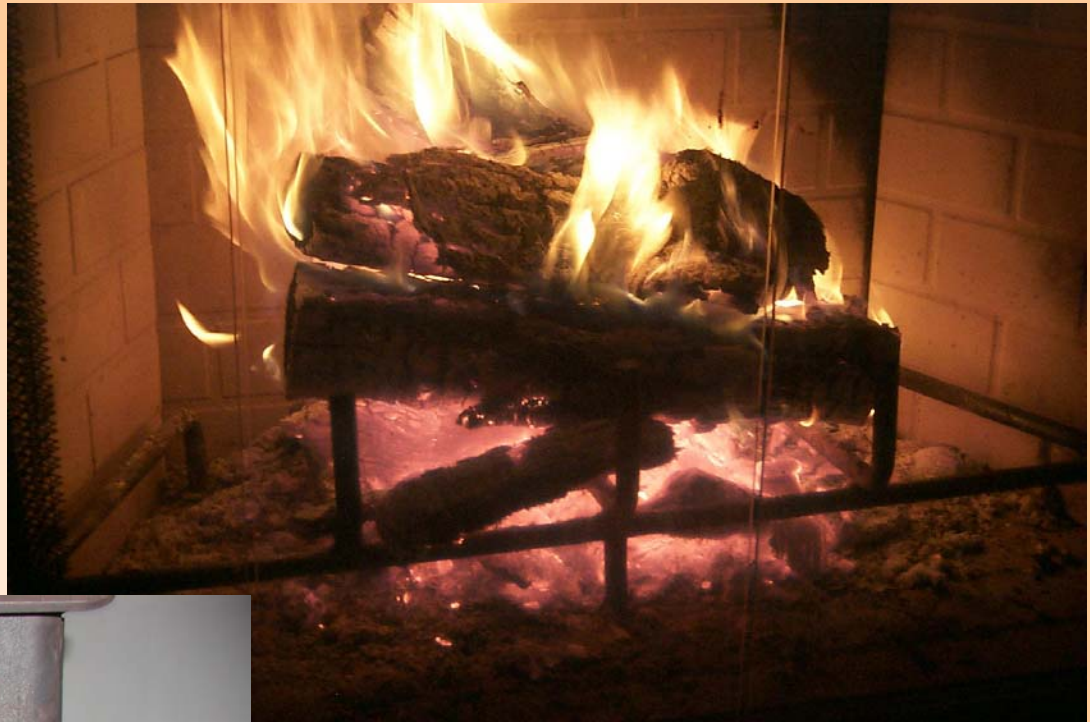
WOODSTOVE

SAMPLE CHARACTERIZATION

Yeast Estrogen Screen
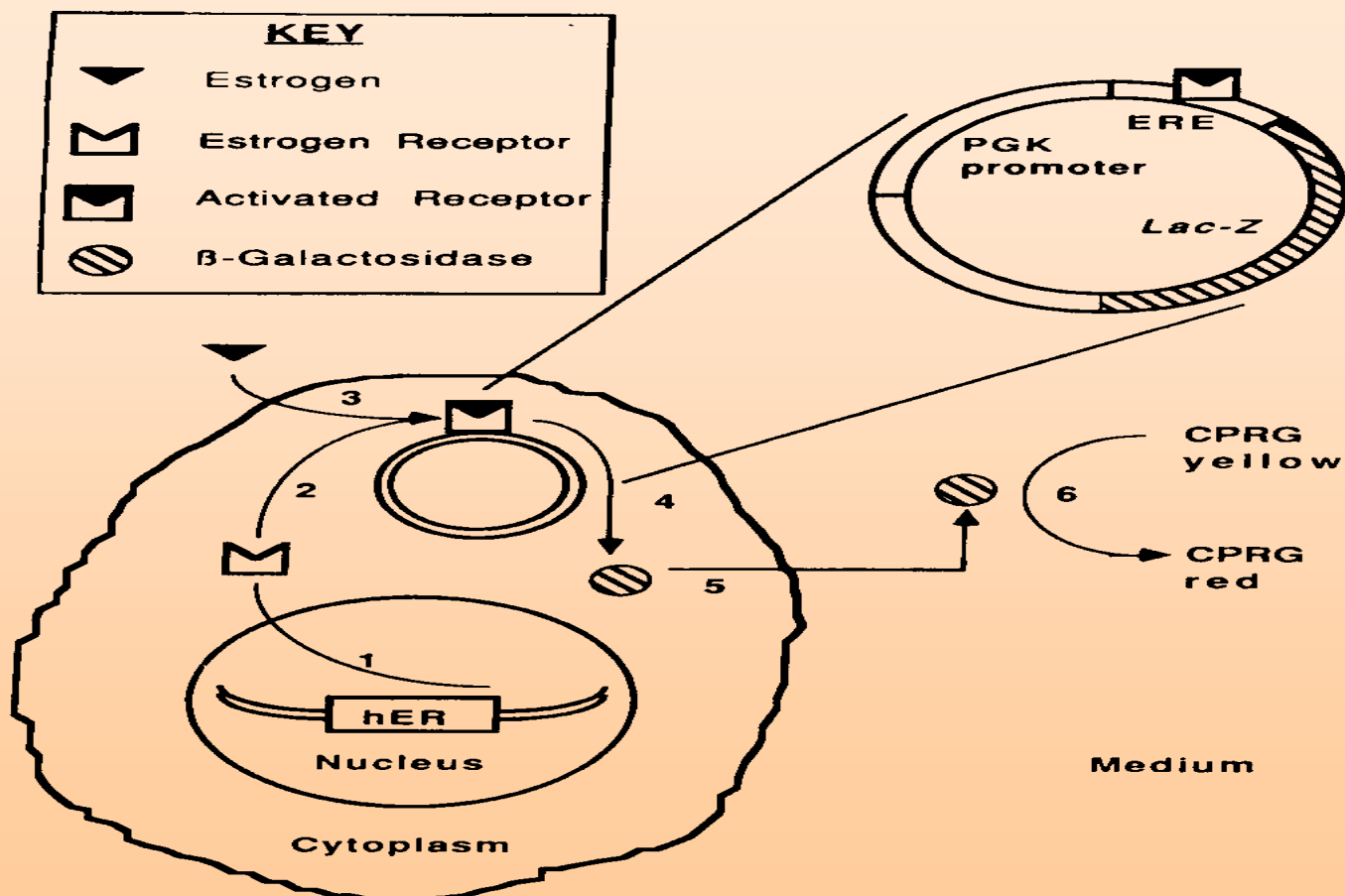
Environmental Estrogens Responding to Yeast Screen
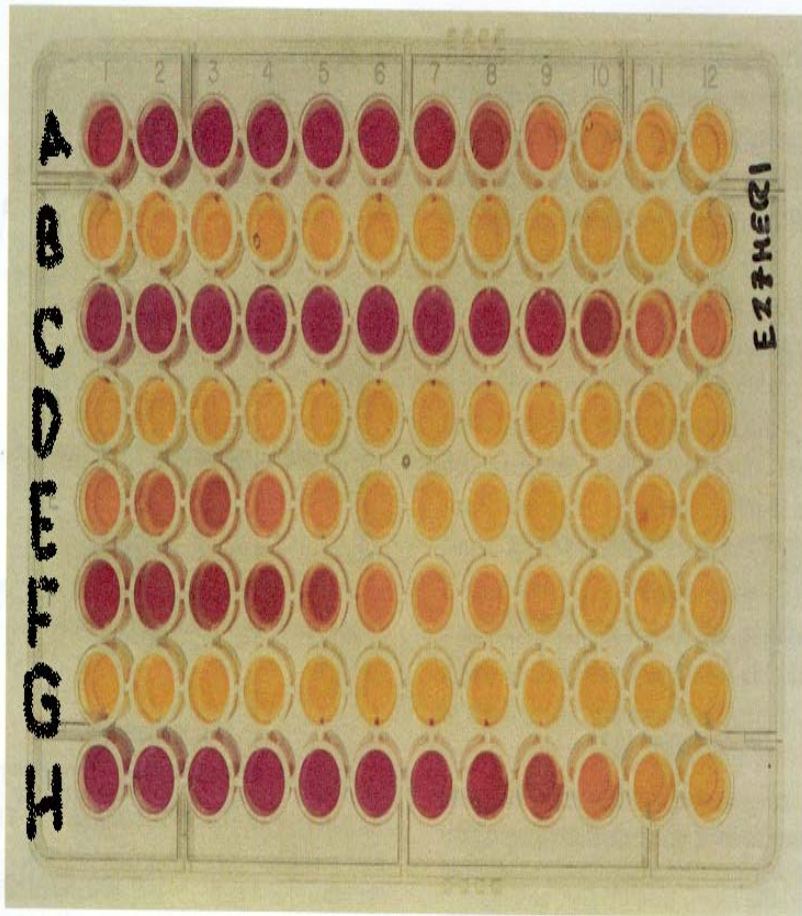
- **Row A = Bisphenol**
  Row C = Genistein
  Row E = Nonyphenol
      Row F = Octylphenol
      Row H = 17β-Estradiol
  Rows B,D,and G (blank)

- **Deep Red Color indicates Estrogenic Activity**
- **Yellow indicates Background (β-gal)**

Gas Chromatography/Mass Spectroscopy
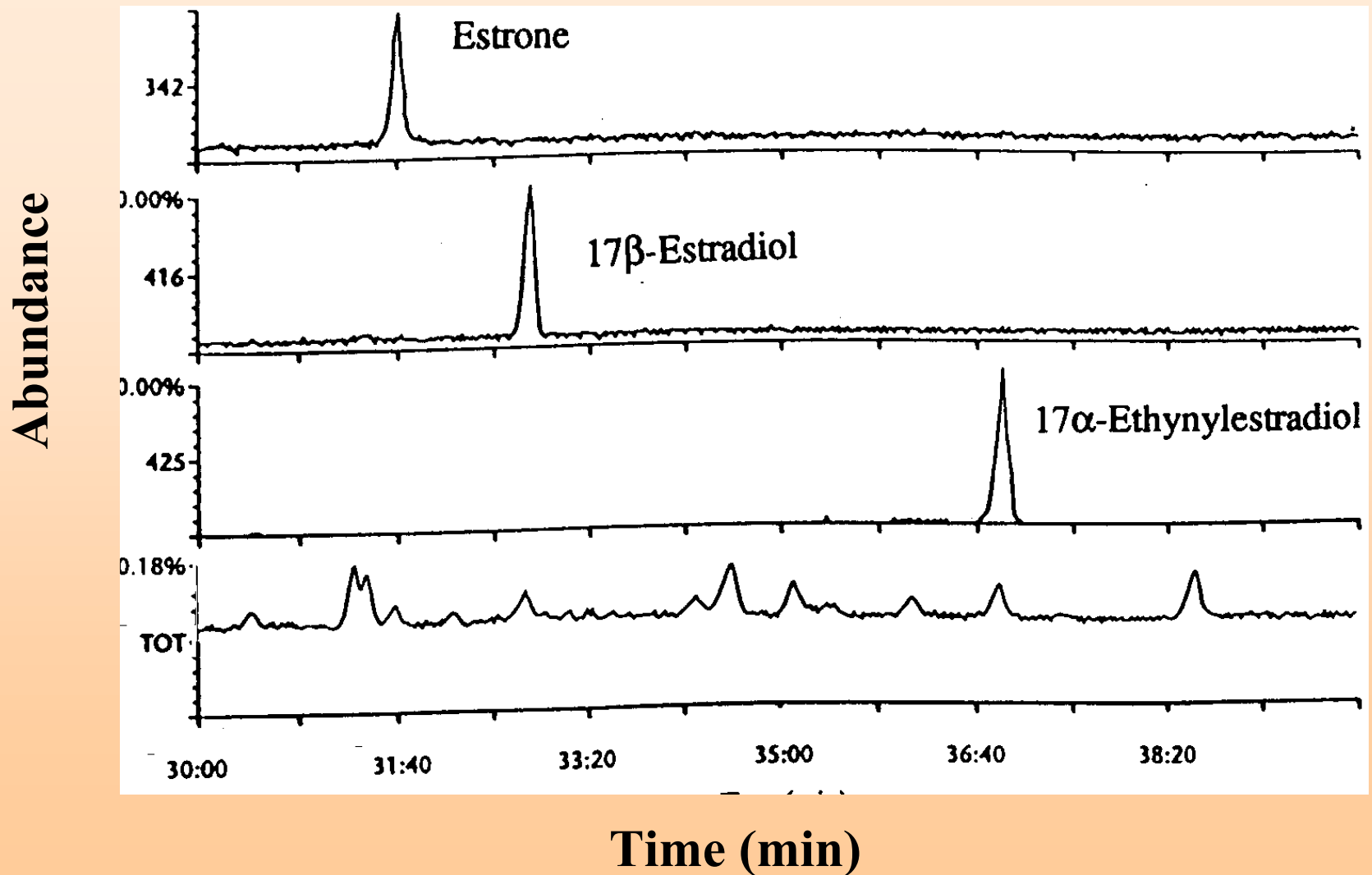
Combustion Pollutant Analysis via Multidimensional Gas Chromatography (courtesy of UDRI)

Conventional GC-MS

MDGC heartcut of region

F I D

Cryotrap and release

30 m
Non-polar Primary column

4 m

Polar secondary column

MSD

Multidimensional GC Assembly

Ion-trap Mass Spectrometer
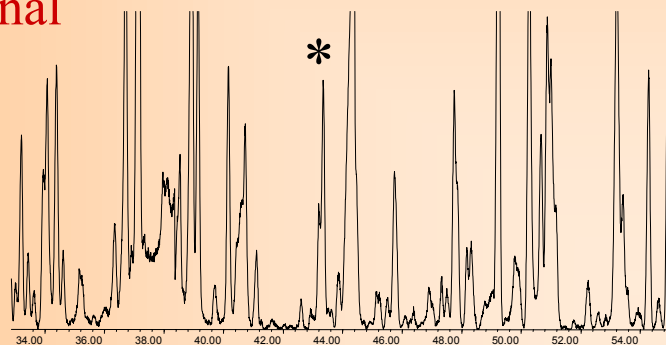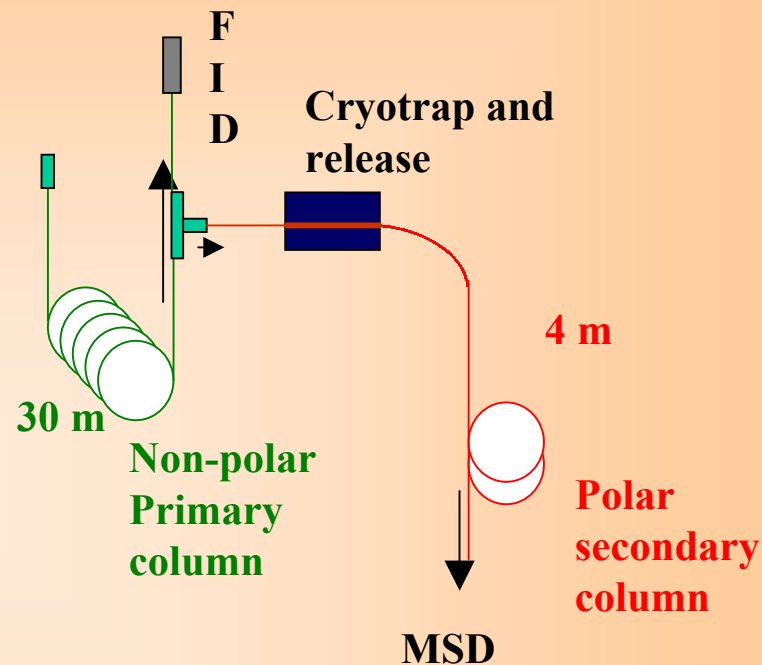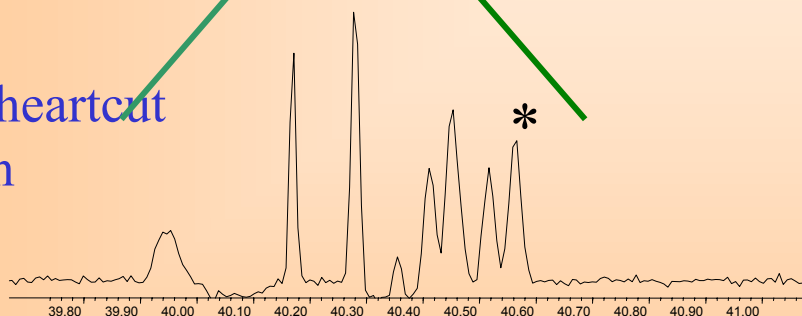
RESULTS

Examples of oxygenates in diesel extracts using MDGC-MS (scanning mode)
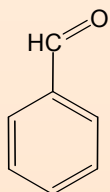
- Benzaldehyde
- Methylbenzaldehyde
- Dibenzofuran
- Xanthene
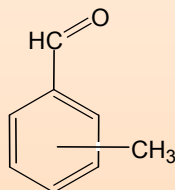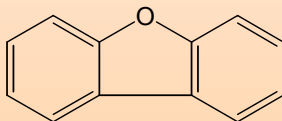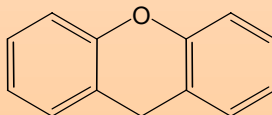
- Hydroxybenzaldehyde
- Naphthalene dione
- Hydroxybiphenyl
- Naphthalene-carboxaldehyde
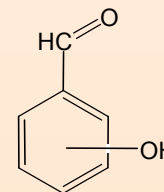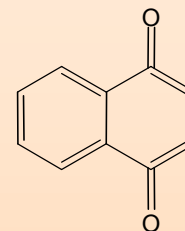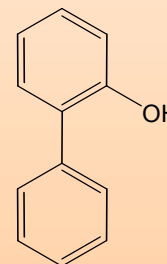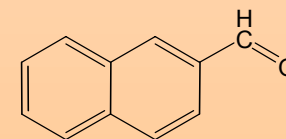
RESULTS

Examples of Oxygenates from Barrel Burn Extract

(   ) denotes Match Quality out of 100

- hydroxy cyclopentanone (7)
- benzaldehyde (87)
- substituted cyclohexanone (72)
- phenol (80)
- methyl quinol (90)
- alkyl phenols (72 - 91)
- methoxy methyl phenol (93)
- hydroxy phenyl butadiene (64)
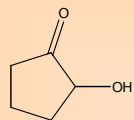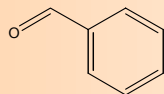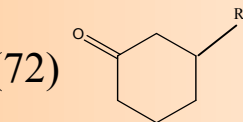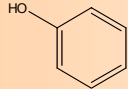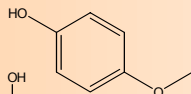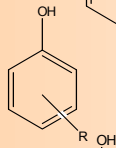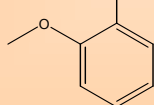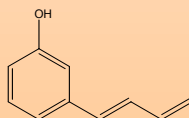
- benzene ethanol 3-methoxy (52)
- benzoic acid (64)
- 4-ethyl-2-methoxy phenol (90)
- benzendiol (90)
- dimethyl anisole (27)
- eugenol (96)
- ethyl vanillin (5)
- methoxy propenyl phenol (90)
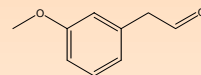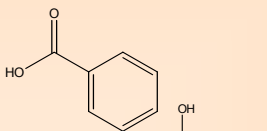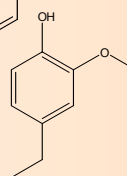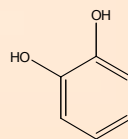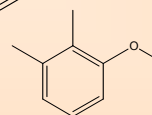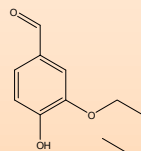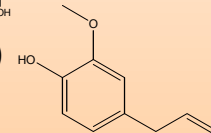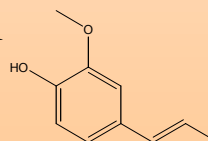
- dihydroxy dimethyl benzaldehyde (5)
- long chain carboxylic acids
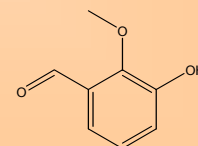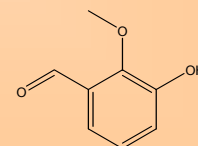- Hydroxy methoxy phenyl ethanone (72)
- hydroxy methoxy phenyl propanone
- methyl benzenediol (78)
- methoxy propyl phenol (64)
- vanillin (78)
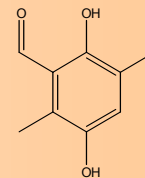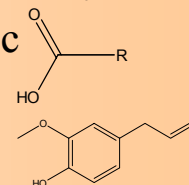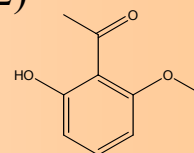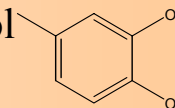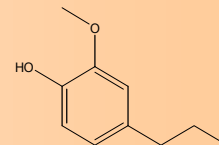
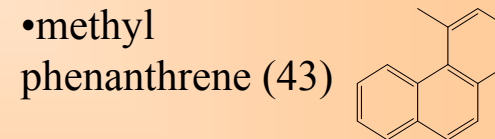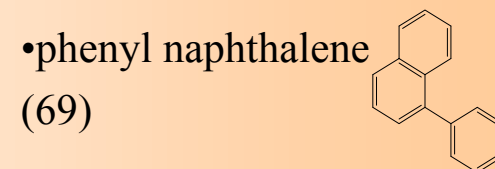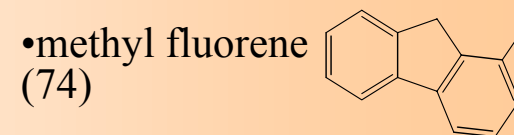# RESULTS

Examples of PAH from Barrel Burn Extract

(   ) denotes Match Quality out of 100

- fluoro-biphenyl (72)

- biphenyl (83)

- me-biphenyl (80)

- dimethyl phenanthrene (64)

- tetramethyl phenanthrene (38)

- biphenylene (72)
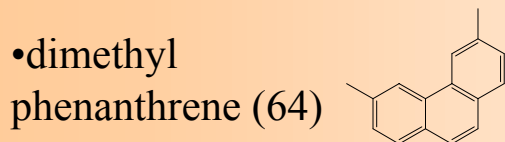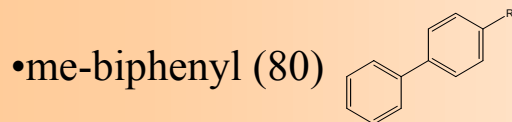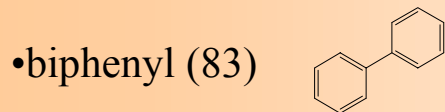
- acenaphthalene (80)

- bibenzyl (74)

- phenanthrene or anthracene (72)

- fluoranthene or pyrene (72)

- vinyl naphthalene (48)

- fluorene (90)

- methyl fluorene (74)

- phenyl naphthalene (69)

- methyl phenanthrene (43)
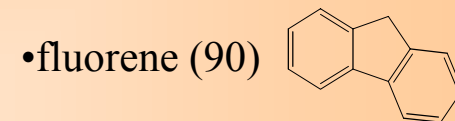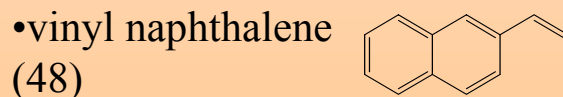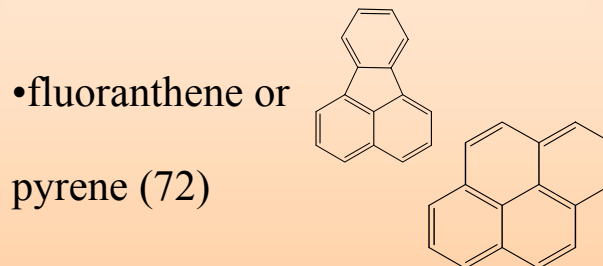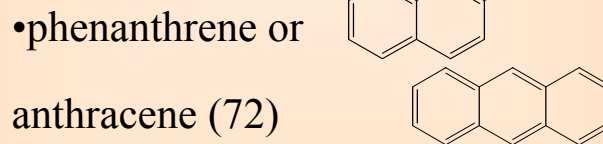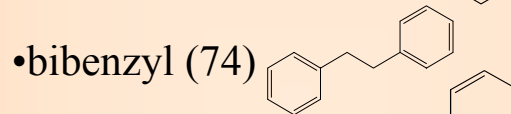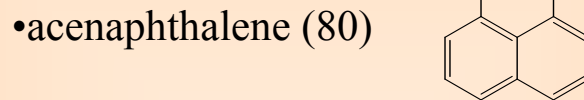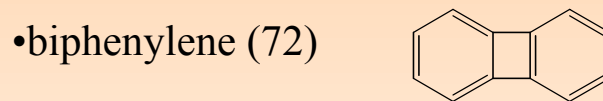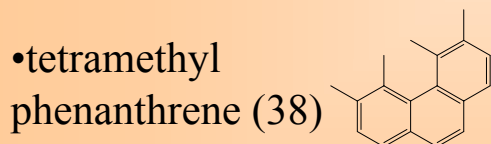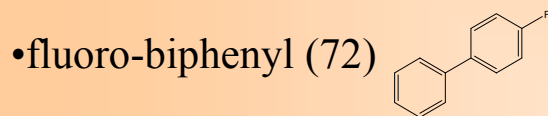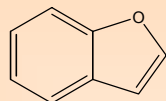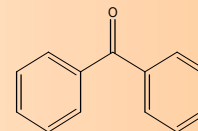
RESULTS

Examples of Oxy-PAH from Barrel Burn Extract

(   ) denotes Match Quality out of 100

•benzofuran (83)

•methyl benzofuran (72)
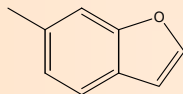
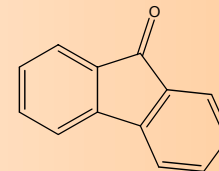•phthalic anhydride (86)
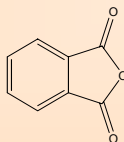
•benzophenone (87)

•fluoren-one (72)

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